DISCHARGE METHODOLOGIES FOR LITHIUM/SILVER VANADIUM OXIDE CELLS TO MANAGE VOLTAGE DELAY AND PERMANENT RDC GROWTH REGION

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority based on provisional application Serial No. 60/405,173, filed August 22, 2002.

BACKGROUND OF INVENTION

1. Field of the Invention

The present invention generally relates to the conversion of chemical energy to electrical energy. More particularly, this invention relates to an alkali metal electrochemical cell having reduced voltage delay and Rdc growth. A preferred couple is a lithium/silver vanadium oxide (Li/SVO) cell. In such cells, it is desirable to reduce voltage delay and permanent or irreversible Rdc growth at about 35% to 70% of depth-of-discharge (DOD) where these phenomena typically occur.

2. Prior Art

Voltage delay is a phenomenon typically exhibited in a lithium/silver vanadium oxide cell that has been depleted of about 35% to 70% of its capacity and is subjected to high current pulse discharge applications. The voltage response of a cell that does not exhibit voltage delay during the application of a short duration pulse or pulse train has distinct features. First, the cell potential decreases

throughout the application of the pulse until it reaches a minimum at the end of the pulse, and second, the minimum potential of the first pulse in a series of pulses is higher than the minimum potential of the last pulse.

On the other hand, the voltage response of a cell that exhibits voltage delay during the application of a short duration pulse or during a pulse train can take one or both of two forms. One form is that the leading edge potential of the first pulse is lower than the end edge potential of the first pulse. In other words, the voltage of the cell at the instant the first pulse is applied is lower than the voltage of the cell immediately before the first pulse is removed. The second form of voltage delay is that the minimum potential of the first pulse is lower than the minimum potential of the last pulse when a series of pulses have been applied.

Thus, decreased discharge voltages and the existence of voltage delay are undesirable characteristics of an alkali metal/silver vanadium oxide cell subjected to current pulse discharge conditions in terms of their influence on devices such as implantable medical devices including pacemakers and cardiac defibrillators. Depressed discharge voltages and voltage delay are undesirable because they limit the effectiveness and even the proper functioning of both the cell and the associated electrically powered device under current pulse discharge conditions.

Therefore, there is a need for a lithium/silver vanadium oxide cell that is dischargeable to deliver the high capacity needed for powering implantable medical devices and the like, but that experiences little, if any, voltage delay and Rdc growth during pulse discharging, especially at about 35% to 70% DOD.

SUMMARY OF THE INVENTION

It is known that reforming implantable defibrillator capacitors at least partially restores and preserves their charging efficiency. An industry-recognized standard is to reform implantable capacitors by pulse discharging the connected electrochemical cell about once every three months throughout the useful life of the medical device. Thus, the basis for the present invention is driven by the desire to substantially reduce, if not completely eliminate, voltage delay and Rdc growth in a Li/SVO cell, while at the same time periodically reforming the connected capacitors to maintain them at their rated breakdown voltages. Methodologies for significantly minimizing, if not entirely eliminating, the occurrence of voltage delay and Rdc growth in the about 35% to 70% DOD region by subjecting Li/SVO cells to novel discharge regimes are described.

These and other objects of the present invention will become increasingly more apparent to those skilled in the art by reference to the following description and to the appended drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph constructed from the average discharge results of two Li/SVO cell groups, one pulse discharged under a 24 month ADD test at 50°C, which is an accelerated test that simulates a 60 month ADD test at 37°C, the other accelerated pulse discharged according to a methodology of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term depth-of-discharge (DOD) is defined as the ratio of delivered capacity to theoretical capacity times 100.

The term "pulse" means a short burst of electrical current of significantly greater amplitude than that of a pre-pulse current immediately prior to the pulse. A pulse train consists of at least one pulse of electrical current. If the pulse train consists of more than one pulse, they are delivered in relatively short succession with or without open circuit rest between the pulses. An exemplary pulse train may consist of four 10-second pulses (23.2 mA/cm^2) with about a 10 to 30 second rest, preferably about 15 second rest, between each pulse. A typically used range of current densities for cells powering implantable medical devices is from about 15 mA/cm^2 to about 50 mA/cm^2, and more preferably from about 18 mA/cm^2 to about 35 mA/cm^2. Typically, a 10 second pulse is suitable for medical implantable applications. However, it could be significantly shorter or longer depending on the specific cell design and chemistry. Current densities are based on square centimeters of the cathode electrode.

An electrochemical cell that possesses sufficient energy density and discharge capacity required to meet the vigorous requirements of implantable medical devices comprises an anode of a metal selected from Groups IA, IIA and IIIB of the Periodic Table of the Elements. Such anode active materials include lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example, Li—Si, Li—Al, Li—B and Li—Si—B alloys and intermetallic compounds. The preferred anode comprises lithium. An alternate anode comprises a lithium alloy such

as a lithium-aluminum alloy. The greater the amounts of
aluminum present by weight in the alloy, however, the lower
the energy density of the cell.

The form of the anode may vary, but preferably the
anode is a thin metal sheet or foil of the anode metal,
pressed or rolled on a metallic anode current collector,
i.e., preferably comprising titanium, titanium alloy or
nickel, to form an anode component. Copper, tungsten and
tantalum are also suitable materials for the anode current
collector. In the exemplary cell of the present invention,
the anode component has an extended tab or lead of the same
material as the anode current collector, i.e., preferably
nickel or titanium, integrally formed therewith such as by
welding and contacted by a weld to a cell case of conductive
metal in a case-negative electrical configuration.
Alternatively, the anode may be formed in some other
geometry, such as a bobbin shape, cylinder or pellet to
allow an alternate low surface cell design.

The electrochemical cell of the present invention
further comprises a cathode of electrically conductive
material that serves as the counter electrode. The cathode
is preferably of solid materials having the general formula
$SM_xV_2O_y$ where SM is a metal selected from Groups IB to VIIB
and VIII of the Periodic Table of Elements, and wherein x is
about 0.30 to 2.0 and y is about 4.5 to 6.0 in the general
formula. By way of illustration, and in no way intended to
be limiting, one exemplary cathode active material comprises
silver vanadium oxide having the general formula $Ag_xV_2O_y$ in
either its β-phase having x = 0.35 and y = 5.8, γ-phase
having x = 0.74 and y = 5.37, or ε-phase having x = 1.0 and
y = 5.5, and combinations of phases thereof.

Before fabrication into an electrode for incorporation
into an electrochemical cell according to the present

invention, the cathode active material is preferably mixed
with a binder material such as a powdered fluoro-polymer,
more preferably powdered polytetrafluoroethylene or powdered
polyvinylidene fluoride present at about 1 to about 5 weight
percent of the cathode mixture. Further, up to about 10
weight percent of a conductive diluent is preferably added
to the cathode mixture to improve conductivity. Suitable
materials for this purpose include acetylene black, carbon
black and/or graphite or a metallic powder such as powdered
nickel, aluminum, titanium, stainless steel, and mixtures
thereof. The preferred cathode active mixture thus includes
a powdered fluoro-polymer binder present at a quantity of at
least about 3 weight percent, a conductive diluent present
at a quantity of at least about 3 weight percent and from
about 80 to about 99 weight percent of the cathode active
material.

Cathode components for incorporation into the cell may
be prepared by rolling, spreading or pressing the cathode
active mixture onto a suitable current collector selected
from the group consisting of stainless steel, titanium,
tantalum, platinum, nickel, and gold. Cathodes prepared as
described above may be in the form of one or more plates
operatively associated with at least one or more plates of
anode material, or in the form of a strip wound with a
corresponding strip of anode material in a structure similar
to a "jellyroll".

In order to prevent internal short circuit conditions,
the cathode is separated from the Group IA, IIA or IIIB
anode material by a suitable separator material. The
separator is of electrically insulative material, and the
separator material also is chemically unreactive with the
anode and cathode active materials and both chemically
unreactive with and insoluble in the electrolyte. In

addition, the separator material has a degree of porosity
sufficient to allow flow therethrough of the electrolyte
during the electrochemical reaction of the cell.
Illustrative separator materials include fabrics woven from
fluoropolymeric fibers including polyvinylidine fluoride,
polyethylenetetrafluoroethylene, and
polyethylenechlorotrifluoroethylene used either alone or
laminated with a fluoropolymeric microporous film, non-woven
glass, polypropylene, polyethylene, glass fiber materials,
ceramics, polytetrafluoroethylene membrane commercially
available under the designation ZITEX (Chemplast Inc.),
polypropylene membrane commercially available under the
designation CELGARD (Celanese Plastic Company, Inc.), a
membrane commercially available under the designation
DEXIGLAS (C.H. Dexter, Div., Dexter Corp.), and a membrane
commercially available under the designation TONEN.

The electrochemical cell of the present invention
further includes a nonaqueous, ionically conductive
electrolyte serving as a medium for migration of ions
between the anode and the cathode electrodes during
electrochemical reactions of the cell. The electrochemical
reaction at the electrodes involves conversion of ions in
atomic or molecular forms that migrate from the anode to the
cathode. Thus, suitable nonaqueous electrolytes are
substantially inert to the anode and cathode materials, and
they exhibit those physical properties necessary for ionic
transport, namely, low viscosity, low surface tension and
wettability.

A suitable electrolyte has an inorganic, ionically
conductive salt dissolved in a mixture of aprotic organic
solvents comprising a low viscosity solvent and a high
permittivity solvent. In the case of an anode comprising
lithium, preferred lithium salts include $LiPF_6$, $LiBF_4$,

$LiAsF_6$, $LiSbF_6$, $LiClO_4$, LiO_2, $LiAlCl_4$, $LiGaCl_4$, $LiC(SO_2CF_3)_3$, $LiN(SO_2CF_3)_2$, $LiSCN$, LiO_3SCF_3, $LiC_6F_5SO_3$, LiO_2CCF_3, $LiSO_6F$, $LiB(C_6H_5)_4$, $LiCF_3SO_3$, and mixtures thereof.

Low viscosity solvents useful with the present invention include esters, linear and cyclic ethers and dialkyl carbonates such as tetrahydrofuran (THF), methyl acetate (MA), diglyme, trigylme, tetragylme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), 1-ethoxy,2-methoxyethane (EME), ethyl methyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, diethyl carbonate, dipropyl carbonate, and mixtures thereof. High permittivity solvents include cyclic carbonates, cyclic esters and cyclic amides such as propylene carbonate (PC), ethylene carbonate (EC), butylene carbonate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, γ-valerolactone, γ-butyrolactone (GBL), N-methyl-2-pyrrolidone (NMP), and mixtures thereof. In the present invention, the preferred anode is lithium metal and the preferred electrolyte is 0.8M to 1.5M $LiAsF_6$ or $LiPF_6$ dissolved in a 50:50 mixture, by volume, of propylene carbonate and 1,2-dimethoxyethane.

The preferred form of the electrochemical cell is a case-negative design wherein the anode/cathode couple is inserted into a conductive metal casing connected to the anode current collector, as is well known to those skilled in the art. A preferred material for the casing is stainless steel, although titanium, mild steel, nickel, nickel-plated mild steel and aluminum are also suitable. The casing header comprises a metallic lid having a sufficient number of openings to accommodate the glass-to-metal seal/terminal pin feedthrough for the cathode electrode. The anode electrode is preferably connected to the case or the lid. An additional opening is provided for

electrolyte filling. The casing header comprises elements
having compatibility with the other components of the
electrochemical cell and is resistant to corrosion. The
cell is thereafter filled with the electrolyte solution
described hereinabove and hermetically sealed such as by
close-welding a stainless steel plug over the fill hole, but
not limited thereto. The cell of the present invention can
also be constructed in a case-positive design.

An exemplary implantable medical device powered by a
Li/SVO cell is a cardiac defibrillator, which requires a
power source for a generally medium rate, constant
resistance load component provided by circuits performing
such functions as, for example, the heart sensing and pacing
functions. This requires electrical current of about 1
microampere to about 100 milliamperes. From time-to-time,
the cardiac defibrillator may require a generally high rate,
pulse discharge load component that occurs, for example,
during charging of a capacitor in the defibrillator for the
purpose of delivering an electrical shock therapy to the
heart to treat tachyarrhythmias, the irregular, rapid
heartbeats that can be fatal if left uncorrected. This
requires electrical current of about 1 ampere to about 4
amperes.

In order to test Li/SVO cells for their electrochemical
characteristics, several accelerated discharge regimes are
commonly used in the industry. One consists of discharging
a Li/SVO cell under a 17.4 kΩ load with superimposed pulse
trains applied every 60 days. The pulse trains consist of
four 2.0 amp pulses of constant current, each of 10-second
duration with about 15 seconds rest between each pulse. One
such pulse train is superimposed on the background load
about every 2 months. This type of discharge is termed 1
year accelerated discharge data (1 Year ADD). Table 1 lists

other industry standard ADD tests and the interval between
each pulse train. The pulse intervals listed in Table 1 are
applicable for tests performed at 37°C.

                              Table 1

           Test Type   Pulse Interval

           1 Year ADD   2 months
           3 Year ADD   4 months
           5 Year ADD   6 months
           36 Month ADD   3 months
           60 Month ADD   5 months

     One issue relative to a Li/SVO cell is the existence of
voltage delay and permanent Rdc growth starting at about 35%
to 70% DOD. Voltage delay and Rdc growth are believed to be
associated with anode surface film formation, which is
influenced by the manner the cell is discharged. From
extensive modeling studies with Li/SVO cells under the
various ADD regimes, it has been discovered that the longer
the ADD test time, the worse voltage delay and Rdc become.
Such parameters as total discharge time to a particular %
DOD, cell current density (mA/cm^2), the number of pulses per
pulse train, and the time between pulse trains, among
others, are believed to affect voltage delay and Rdc growth.

     In actual defibrillator device applications, one very
important parameter is the charge time to achieve a pre-
determined energy for therapy delivery. In other words, the
time to charge a capacitor to a required voltage is affected
by voltage delay and Rdc growth. A typical cardiac
defibrillator requires energy in the range of from about 40

Joules to about 70 Joules per Li/SVO cell for electrical
shock therapy. The relationship is shown below:

$$Energy(J) = I(amp) \times V(volt) \times t(sec.)$$
$$t(s) = Energy\ (J)/IV$$

   If the required delivered energy (J) and pulsing
current (amp) are both defined, then the charge time in
seconds is inversely proportional to the average voltage
under pulsing. Therefore, to maintain a relatively low
charge time, the cell must deliver higher voltage under
pulsing. This requirement is, however, compromised by the
voltage delay and Rdc growth phenomena in the Li/SVO system
at the middle of discharge life region (starting at about
35% DOD). Under severe conditions, cell voltage under
pulsing becomes so low that the charge time is considered
too long for the required therapy. This results in
shortened device longevity. Since voltage delay and Rdc
growth start at about 35% to 40% DOD, it is possible that
only about 40% of the theoretical capacity of a particular
Li/SVO cell is actually delivered. The remaining capacity
is wasted. Therefore, the present invention is directed to
methodologies designed to avoid or get around the voltage
delay and Rdc growth region in a Li/SVO cell.
   A cardiac defibrillator essentially consists of an
electrochemical cell as a power source for charging at least
one electrolytic capacitor to deliver the electrical shock
therapy to the patient's heart. Microprocessors powered by
the cell perform the heart sensing and pacing functions and
initiate capacitor charging to deliver the electrical shock
therapy. Not only does the Li/SVO cell experience voltage
delay and Rdc growth problems at about 35% DOD as explained
above, but electrolytic capacitors can experience

degradation in their charging efficiency after long periods
of inactivity. It is believed that the anodes of
electrolytic capacitors, which are typically of aluminum or
tantalum, develop microfractures after extended periods of
non-use. These microfractures consequently result in
extended charge times and reduced breakdown voltages.
Degraded charging efficiency ultimately requires the Li/SVO
cell to progressively expend more and more energy to charge
the capacitors for providing therapy.

To repair this degradation, microprocessors controlling
the implantable medical device are programmed to regularly
charge the electrolytic capacitors to or near a maximum-
energy breakdown voltage (the voltage corresponding to
maximum energy) before discharging them internally through a
non-therapeutic load. The capacitors can be immediately
discharged once the maximum-energy voltage is reached or
they can be held at maximum-energy voltage for a period of
time, which can be rather short, before being discharged.
These periodic charge-discharge or charge-hold-discharge
cycles for capacitor maintenance are called "reforms."
Reforming implantable defibrillator capacitors at least
partially restores and preserves their charging efficiency.

An industry-recognized standard is to reform
implantable capacitors by pulse discharging the connected
electrochemical cell about once every three months
throughout the useful life of the medical device, which is
typically dictated by the life of the cell. Thus, the basis
for the present invention is driven by the desire to
substantially reduce, if not completely eliminate, voltage
delay and Rdc growth in a Li/SVO cell while at the same time
periodically reforming the connected capacitors to maintain
them at their rated breakdown voltages. Therefore, the
present invention relates to methodologies for significantly

minimizing, if not entirely eliminating, the occurrence of voltage delay and irreversible Rdc growth in Li/SVO cells by subjecting them to novel discharge regimes.

The first discharge methodology comprises more frequent pulses being applied to a Li/SVO cell than the present industry standard of about once every three months deemed sufficient for capacitor reform. The current pulses can either be delivered to the device being powered by the cell or to a secondary "dummy" circuit.

In the first methodology, the Li/SVO cell is discharged to deliver a pulse train at least about once every one day to about once every 60 days, more preferably once every seven days to about once every four weeks. High current pulsing preferably consists of periodic pulse trains of four 10-second 2 to 3 amp pulses (15 mA/cm^2 to 50 mA/cm^2) with 15 seconds rest between each pulse. At the very minimum, the cell delivers a pulse train about once every seven days to four weeks in the about 15% to about 80% DOD region, more preferably in the about 20% to about 75% DOD region, and most preferably in the about 25% to about 70% DOD region. However, it is within the purview of the present invention to subject the cell to pulse trains of reduced interim intervals, i.e. at least about once every seven days to about four weeks, for the cell's remaining useful life once pulse discharge reform maintenance of the connected capacitors begins. By significantly minimizing voltage delay and Rdc growth, especially in the 35% to 70% DOD region, the time to charge a capacitor is well within the device application threshold. This allows for more practical deliverable energy.

A second methodology according to the present invention is to quickly discharge the cell once it enters the voltage delay region. Discharge is in the form of current pulses

delivered to the device being powered by the cell or to a secondary "dummy" circuit. Such a rapid discharge protocol is designed to remove from about 2% to about 20% of the cell's discharge capacity beginning at about 15% DOD, more preferably beginning at about 20% DOD, and most preferably beginning at about 25% DOD.

A preferred protocol under the second methodology is to discharge the cell under current pulsing to remove about 10% DOD beginning at about 25% DOD in a time period of from about 20 minutes to about 24-hours, then resume the normal discharge regime for capacitor reform maintenance of about once every three months. The 20% to 20% DOD is removed from the cell by adjusting the interval between pulse trains. High current pulsing preferably consists of periodic pulse trains of four 10-second 2 to 3 amp pulses (15 mA/cm^2 to 50 mA/cm^2) with 15 seconds rest between each pulse.

In this manner, the region of severe voltage delay and Rdc growth is by-passed. In the remaining discharge region of about 45% to 80+% DOD, cell Rdc does not grow significantly, which, in turn, translates into higher pulse voltages and shorter charge times. Therefore, at least 25% + 35+% = 60+% of theoretical capacity is deliverable as useful energy, instead of just 35% to 40% of theoretical capacity under the traditional discharge regime in the worst case.

The following example describes the manner and process of an electrochemical cell according to the present invention, and set forth the best mode contemplated by the inventors of carrying out the invention.

EXAMPLE I

FIG. 1 is a graph drawn from the average discharge characterization results of two Li/SVO cell groups, each

group having five cells of similar construction and energy density. The cells were periodically discharged at 50°C under a 16.5 kΩ load with superimposed pulse trains applied every 63 days. The pulse trains consisted of two 2.5 amps, 10-second pulses with 15 seconds rest between each pulse. This type of discharge is termed 24 month accelerated discharge data (24MADD), which simulates 60MADD at 37°C with pulse intervals of 154 days. The cells used to construct curve 10 were subjected to this protocol throughout the entire test. However, the cells used to construct curve 12 were switched to a more rapid discharge protocol after the fourth pulse train. Then, they were pulse discharged every 14 days until the end of the test.

It can be seen that in the case of the cells of curve 10, the charge time to 60 joules at pulse 1 end significantly increased after about 900 mAh of capacity was removed. This corresponds to a DOD of about 35%. However, the cells of curve 12 experienced significantly less charge time than the other cells to a similar delivered energy. The conclusion is that according to the first discharge methodology of the present invention, starting at about 25% DOD to about 35% DOD, voltage delay and Rdc growth in a lithium/transition metal oxide cell, and particularly a Li/SVO cell, are significantly reduced by more frequently pulse discharging the cell than the current industry standard of about once every three months, which is deemed satisfactory for implantable capacitor reform.

It should be pointed out that conducting an ADD test at 50°C accelerates discharge about 2.46 times in comparison to the same test conducted at 37°C.

It is appreciated that various modifications to the present inventive concepts described herein may be apparent to those of ordinary skill in the art without departing from

the spirit and scope of the present invention as defined by
the herein appended claims.